

# Short to long-range charge-transfer excitations in the zincbacteriochlorin-bacteriochlorin complex: a Bethe-Salpeter study

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We study using the Bethe-Salpeter formalism the excitation energies of the zincbacteriochlorin-bacteriochlorin dyad, a paradigmatic photosynthetic complex. In great contrast with standard time-dependent density functional theory calculations with (semi)local kernels, charge transfer excitations are correctly located above the intramolecular Q-bands transitions found to be in excellent agreement with experiment. Further, the asymptotic Coulomb behavior towards the true quasiparticle gap for charge transfer excitations at long distance is correctly reproduced, showing that the present scheme allows to study with the same accuracy intramolecular and charge transfer excitations at various spatial range and screening environment without any adjustable parameter.

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Photoinduced charge transfer excitations, namely the jump upon photon absorption of an electron from a donor to an acceptor site, is a fundamental process that governs photosynthetic processes in plants and bacteria,<sup>1</sup> or the quantum efficiency in organic or hybrid photovoltaic cells.<sup>2</sup> Such non-local excitations are also an important current theoretical issue since it is now well recognized that the time-dependent density functional theory (TDDFT)<sup>3</sup> encounters severe problems to describe such excitations when standard (semi)local kernels, or even hybrid kernels mixing some amount of exact exchange, are being used.<sup>4</sup> Besides organic systems, similar problems have been identified in the case of extended Wannier excitons in semiconductors where the large effective excitonic radius leads to a weak average overlap between the hole and the electron.<sup>5</sup>

The bacteriochlorin molecule is closely related to the magnesium-containing bacteriochlorophyll system. Due to its importance as a paradigmatic photosynthetic complex, and as one of the earliest charge-transfer system for which the TDDFT difficulties have been unraveled and discussed,<sup>4</sup> the zinc-bacteriochlorin/bacteriochlorin (ZnBC-BC) complex (see Fig. 1) has been studied by a variety of approaches, including TDDFT with local,<sup>4,6,7</sup> hybrid,<sup>7</sup> Coulomb attenuated hybrid<sup>7</sup> functionals, constrained  $\Delta$ SCF DFT calculations,<sup>8</sup> and quantum chemistry many-body wavefunctions techniques such as a combination of  $\Delta$ SCF DFT and single excitation configuration interaction (CIS) technique,<sup>4</sup> or a more elaborate CIS(D) approach including various scaled perturbative double-excitation correlation corrections.<sup>9</sup>

In two recent studies,<sup>10,11</sup> charge transfer (CT) excitations in small donor/acceptor complexes, combining tetracyanoethylene with acene derivatives, were studied with the *GW* approximation and Bethe-Salpeter (BSE) equation within many-body perturbation theory.<sup>12</sup> Excellent agreement with gas phase experiments<sup>13</sup> was obtained for the lowest CT excitation energy with a mean absolute error of about 0.1 eV.<sup>11</sup> Such an accuracy compared well with recent TDDFT calculations with opti-

mized range-separated functionals,<sup>14</sup> while TDDFT calculations with standard PBE or even non-local B3LYP kernels<sup>15,16</sup> were shown to lead to discrepancies of several eV with CT states located at much too low energy.<sup>14</sup>

In this work, we study the optical absorption spectrum of the ZnBC-BC complex using the *GW*-BSE many-body perturbation theories. We show that intramolecular excitations are in excellent agreement with experiment, and that the charge-transfer excitations are correctly located above the intramolecular Q-bands transitions, in great contrast with TDLDA calculations which locate the charge-transfer excitations about 1.7 eV below the *GW*-BSE value. It is further shown that the *GW*-BSE framework correctly reproduces the long-range energy behavior of the charge transfer excitations, a feature shared only with the scaled CIS(D) correlated quantum chemistry approach. The importance of going beyond the Tamm-Dancoff approximation is further discussed.

Our calculations are based on a recently developed auxiliary even-tempered Gaussian-basis<sup>17</sup> implementation of the *GW*<sup>18–21</sup> and BSE<sup>22–26</sup> formalisms, the FIESTA package, implementing contour deformation techniques for the correlation contribution to the self-energy.<sup>11,27</sup> The needed two-body operators such as the susceptibilities, bare/screened Coulomb potentials and self-energies, are expressed on an atom-centered Gaussian-basis containing six  $\exp(-\alpha r^2)$  gaussian for the radial part of each (*s*, *p*, *d*)-channels, with an even tempered distribution of localization coefficient  $\alpha$  ranging from 0.1 to 3.2 a.u. Such a basis derives from previous studies<sup>27–29</sup> but with additional diffuse orbitals.

The needed starting single-particle states are taken to be the Kohn-Sham DFT/LDA eigenstates generated by the SIESTA package<sup>30</sup> using a large triple-zeta plus double polarization basis (TZDP).<sup>31</sup> It was shown recently that the combination of a TZDP basis for describing Kohn-Sham occupied and virtual states, with the above described auxiliary bases, was leading to charge-transfer excitation energies in excellent agreement with planewave *GW*-BSE calculations.<sup>11</sup> For the isolated ZnBC and BC

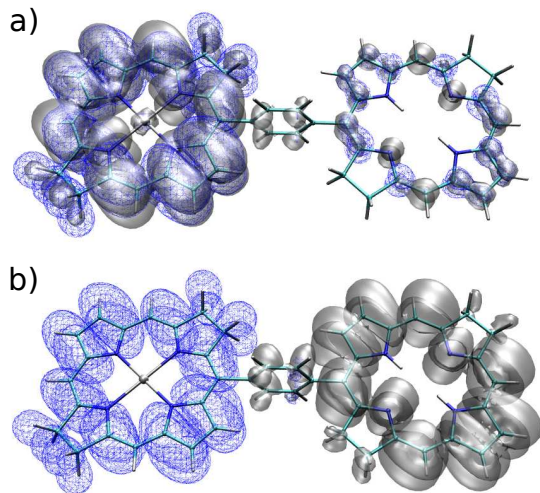


FIG. 1: (Color online) Symbolic representation of the (1,4)-phenylene-linked zincbacteriochlorin-bacteriochlorin complex. Isocontour representation of the (grey) hole-averaged electron and (blue) electron-average hole distributions (see text) for the lowest (a) ZnBC  $Q_x$  excitation and (b) ZnBC  $\rightarrow$  BC charge-transfer excitation.

molecules, for which experimental data are available,<sup>32,33</sup> we relax the molecules at the all-electron B3LYP 6-311G(d) level.<sup>34</sup> However, for the ZnBC-BC bridged complex, we adopt the geometry provided in Ref. 4, and used in subsequent studies,<sup>7-9</sup> as a mean to properly compare to other computational approaches.

In the present many-body framework, one first obtains accurate quasiparticle energies (occupied and virtual electronic energy levels) by using the *GW* formalism. In the case of gas phase organic molecules such as fullerenes, pentacene, PTCDA or porphyrins, it was shown in several recent studies<sup>27,35-37</sup> that the standard single-shot  $G_0W_0$  calculations based on input Kohn-Sham eigenstates with standard local functionals tends to yield too small HOMO-LUMO gaps, even though already much better than the starting Kohn-Sham values. Better results could be consistently obtained for the quasiparticle spectrum of small molecules either by starting from Hartree-Fock<sup>27,38-40</sup>, or hybrid functionals<sup>41</sup> eigenstates, or by performing a full self-consistency on the quasiparticle eigenstates,<sup>39,40</sup> or a limited self-consistency on the eigenvalues only,<sup>11,27,29,37,42</sup> allowing to remove the dependency of the final quasiparticle energies on the starting point eigenstates. This is such an approach that we adopt in the present study, showing here below as in Ref. 11 that excellent agreement with experiment can be obtained for the excitation energies.

In an optical absorption spectrum, the quasiparticle gap is reduced by the electron-hole interaction. In the present MBPT formalism, this excitonic interaction is accounted for by the BSE equations. Namely, the neutral excitation energies can be obtained as the eigen-

values of the BSE  $H^{e-h}$  Hamiltonian<sup>22-26</sup> expressed in the  $\phi_i^e(\mathbf{r})\phi_j^h(\mathbf{r}')$  product basis of the unoccupied  $\phi_i^e$  and occupied  $\phi_j^h$  single-particle states. Of importance for the upcoming discussion, we write the so-called direct term involving the (statically) screened Coulomb potential  $W(\mathbf{r}, \mathbf{r}')$ , noticing that hole and electron states are not taken at the same space position:

$$H_{ij,kl}^{direct} = - \int d\mathbf{r} d\mathbf{r}' \phi_i^e(\mathbf{r}) \phi_j^h(\mathbf{r}') W(\mathbf{r}, \mathbf{r}') \phi_k^e(\mathbf{r}) \phi_l^h(\mathbf{r}'),$$

As compiled in Table I, we first verify that our *GW*-BSE low-lying  $Q_x$  and  $Q_y$  transition<sup>43</sup> energies for the isolated monomers fall within 0.1 eV of the available experimental values. Consistently with previous observations,<sup>28,44</sup> we find that the diagonalization of the full BSE Hamiltonian leads to a red shift which can be as large as 0.35 eV as compared to the *GW*-BSE results in the Tamm-Damcov (TDA) approximation, bringing the calculated transitions in excellent agreement with experiment. Such a good agreement with available experimental data can be taken as an indication of the reliability of the present formalism and of the specific implementation aspects.

Concerning the TDLDA calculations, performed with the same Kohn-Sham states and auxiliary basis, we observe that the agreement with experiment is also satisfactory, even though not as good as the BSE values. Our calculated TDLDA results compare very well with former TD-BLYP calculations.<sup>4,7</sup> Again, this allows to verify that the pseudopotential approximation and the bases we use do not lead to significant errors as compared to all-electron calculations with standard quantum chemistry basis. For intramolecular transitions with large overlap between hole and electron states, the TDDFT approach with standard kernels is a reliable framework.

We now come to the central point of this study, namely the ZnBC-BC CT excitation energies. The charge-transfer nature of a given transition can be easily identified by analyzing the weight of the two-body BSE eigenstates on the  $\phi_{lumo}^e$  and  $\phi_{homo}^h$  one-body eigenstates localized on either molecule. The expectation value of the electron/hole density operator  $\delta(\mathbf{r} - \mathbf{r}_e/\mathbf{r}_h)$  on a given two-body BSE eigenstate allows further to build the corresponding hole/electron-averaged electron/hole distribution. Such a representation is provided in Fig. 1(b) for the ZnBC $\rightarrow$ BC charge-transfer state obtained at the *GW*-BSE (full) level. The charge-transfer nature of such an excited state is apparent.

As shown in Table I, TD-LDA severely underestimates the CT excitation energies which are found to lie significantly below the intramolecular Q-bands. Identical conclusions were found with the BLYP functional.<sup>4,7</sup> Such a behavior can be understood from the analysis of the TDDFT electron-hole coupling terms which vanish for transitions between non-overlapping electron and hole states in the case of (semi)local exchange-correlation kernel. One is then left with the non-interacting diagonal

	TD-DFT (TDA)				GW-BSE		Exp. <sup>c,d</sup>
Transitions	BLYP <sup>a/b</sup>	LDA	B3LYP <sup>b</sup>	CAM-B3LYP <sup>b</sup>	TDA	full	
Isolated BC and ZnBC monomers							
$\pi$ - $\pi^*$ $Q_x$ ZnBC	2.07/2.04	2.09	2.05	1.87	1.94	1.59	1.65
$\pi$ - $\pi^*$ $Q_x$ BC	2.10/2.10	2.10	2.12	1.92	1.90	1.63	1.6
$\pi$ - $\pi^*$ $Q_y$ BC	2.39/2.40	2.45	2.54	2.53	2.38	2.24	2.3
$\pi$ - $\pi^*$ $Q_y$ ZnBC	2.44/2.43	2.47	2.60	2.59	2.29	2.27	2.2
ZnBC-BC phenylene-bridged complex							
$\pi$ - $\pi^*$ $Q_x$ ZnBC	2.05/2.05	2.08	2.41	1.89	1.99	1.69	
$\pi$ - $\pi^*$ $Q_x$ BC	2.09/2.09	2.10	2.43	1.93	2.04	1.73	
$\pi$ - $\pi^*$ $Q_y$ BC	2.38/2.37	2.46	2.79	2.49	2.47	2.35	
$\pi$ - $\pi^*$ $Q_y$ ZnBC	2.42/2.42	2.44	2.83	2.54	2.49	2.34	
CT ZnBC $\rightarrow$ BC	1.33/1.33	1.25	1.96	2.87	2.95	2.95	
CT BC $\rightarrow$ ZnBC	1.46/1.46	1.39	2.12	3.04	3.13	3.13	

TABLE I: Calculated singlet transition energies (in eV) for the isolated monomers and the (1,4)-phenylene-linked ZnBC-BC complex. The present TD-LDA (TDA), GW-BSE (TDA) and GW-BSE (full) results are compared to previous TD-DFT calculations with the BLYP and B3LYP functionals. (TDA) means Tamm-Dancoff approximation, while (full) means full diagonalization mixing resonant and antiresonant transitions. <sup>a</sup>Ref. 4. <sup>b</sup>Ref. 7. <sup>c,d</sup>Refs. 32,33.

part, namely the too small Kohn-Sham HOMO-LUMO gap. Such a situation is slightly improved with the B3LYP functional due to its 20% of exact exchange, but with a residual error as large as 1 eV. This cancellation of the interacting term for non-local charge-transfer excitations does not occur in the BSE formalism since in the  $H_{ij,kl}^{direct}$  interaction term, hole and electron states are not taken at the same position in space and are connected by the non-local screened Coulomb potential  $W(\mathbf{r}, \mathbf{r}')$ .

The GW-BSE CT excitation energies lie well above the intramolecular Q-bands, consistently with TDDFT calculations with optimized (parametrized) CAM-B3LYP functionals<sup>7</sup> and CIS(D) calculations<sup>9</sup> (see analysis below). Concerning the CAM-B3LYP results, with CT states located less than 0.1 eV below the GW-BSE one, to be compared to the  $\sim 1.7$  eV discrepancy with TDLDA, the agreement is very good considering that the needed  $(\alpha, \beta)$  scaling parameters<sup>46</sup> have been trained on a very different set of molecules, the so-called G2 set, and on very different properties, namely ionization energies. These results confirm the agreement already found between GW-BSE and a TDDFT calculation with another optimized range-separated functional (the BNL functional<sup>45</sup>) in the study of small TCNE-acenes complexes, both calculations coming in close agreement with experiment for CT states.<sup>11,14</sup>

The ability of the BSE approach to describe charge-transfer excitations can be further illustrated by studying the long range limit where the BC and ZnBC units are separated by removing the phenylene bridge. The distance  $R$  between the two monomers in the unbridged model dimer is defined in Fig. 2a (Inset).  $R \sim 5.84$  Å is the corresponding distance between the two monomers in the phenylene-bridged complex. Our results are represented in Fig. 2. As expected, intramolecular charge transfer excitations are independent of the distance between the molecules. On the contrary, in the large distance limit, the CT exciton binding energies are found to scale like  $1/D$ , where  $D$  is the dis-

tance between the  $R_1$  and  $R_2$  molecule centres, as indicated in Fig. 2b (thick grey line). In the large  $D$  limit, the direct interaction terms converge to:  $H_{ij,kl}^{direct} \simeq -W(\mathbf{R}_1, \mathbf{R}_2) Q_{ik}^e Q_{jl}^h$ , where  $W(\mathbf{R}_1, \mathbf{R}_2)$  reduces to the bare  $1/|\mathbf{R}_1 - \mathbf{R}_2|$  Coulomb potential for the two molecules in the vacuum<sup>47</sup> and  $Q_{jl}^h = \langle \phi_j^e | \phi_k^e \rangle$ . With  $Q_{ik}^e = \delta_{ik}$  and  $Q_{jl}^h = \delta_{jl}$ , there is no mixing with higher subbands, so that the lowest CT state is primarily composed of the HOMO and LUMO eigenstates in the long distance limit, as verified by analyzing the BSE eigenstates.

Such  $(1/D)$  behavior of the CT excitonic binding energy is the correct asymptotic limit of an electrostatic interaction between opposite charges. In this limit, the CT excitation energies correctly converge towards the non-interacting (diagonal) part of the BSE Hamiltonian, namely the true quasiparticle gap between the concerned hole and electron states as given by the GW calculation. *The ability of the GW-BSE approach to correctly describe without adjustable parameter both intramolecular and short to long-range charge transfer excitations energies, both in finite (molecular) and extended (infinite solids) systems,<sup>48</sup> is a important feature as discussed here below by comparison with previous studies.*

As emphasized above, TD-DFT calculations with local kernels cannot reproduce the long-range electron-hole interaction: the CT energies remain constant and equal to the Kohn-Sham band gap. This is now well documented<sup>4,6,7</sup> and we clearly verify that point with our TDLDA data (see dotted lines below 1.5 eV in Fig. 2). As a dramatic improvement over local kernels, the TD-CAM-B3LYP approach<sup>7</sup> provides a much better agreement with GW-BSE calculations in the short-range limit of the bridged dimer (see above). However, as already noticed in Ref. 7, the  $(\alpha + \beta)/D$  long-range behavior, with  $(\alpha + \beta) = 0.65$ ,<sup>46</sup> cannot reproduce the correct  $1/D$  long-range limit. Similarly, the asymptotic limit of the TD-B3LYP approach would reduce to  $0.2/D$ , thanks to the 20% of exact exchange. This discussion clearly un-



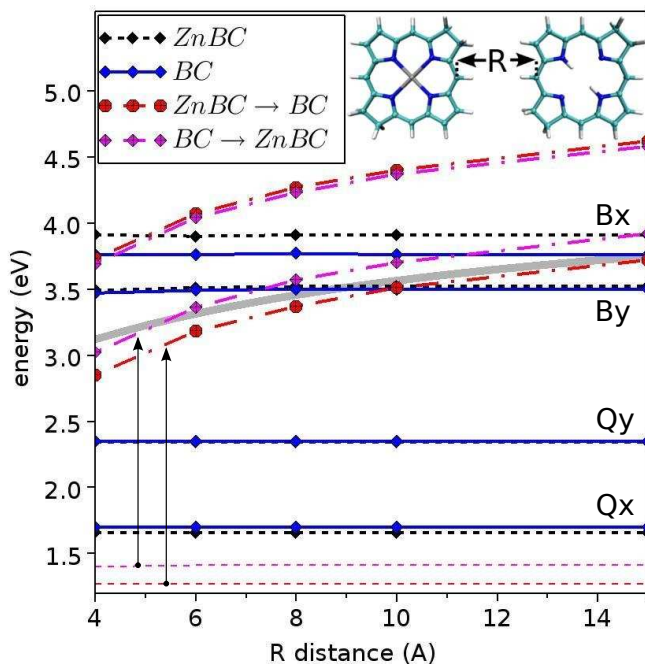


FIG. 2: (Color online) GW-BSE excitation energies as a function of the ZnBC to BC distance  $R$  in the absence of the phenylene bridge as indicated on the atomic representation. The Inset indicates the intramolecular or charge-transfer nature of the represented GW-BSE transitions. The lowest ZnBC  $\rightarrow$  BC CT excitation energy is compared to the  $(E_{Gap}^{GW} - e^2/D)$  “Mulliken” limit (thick grey line), with  $E_{Gap}^{GW}$  the dimer GW quasiparticle band gap in the large  $D$  limit, where  $D$  is the distance between the two molecule centers. For sake of comparison, the TDLDA values for the two low lying CT excitons are indicated by the two non-dispersive dotted lines below 1.5 eV. The two vertical arrows indicate the difference between the TDLDA and GW-BSE values. For completeness, the higher lying intramolecular Soret B-transitions and CT excitations, not detailed in the Table, are also reproduced.

derlines the difficulty of working with fixed parameters functionals performing equally well at any range and in any screening environment (vacuum, solvent, etc.)<sup>47</sup>

As a final comparison, we now analyse the difference with the hybrid single configuration interaction (CIS) approach proposed in the seminal Ref. 4. In the TDA approximation, valid for CT states in the long-range limit, CIS is equivalent to time-dependent Hartree-Fock showing the correct  $1/D$  asymptotic limit for charge transfer excitations, but with an incorrect asymptotic limit given by the donor-HOMO to acceptor-LUMO gap calculated in the absence of correlations. The neglect of correla-

tion in TD-HF was corrected by a distance independent term obtained from DFT  $\Delta$ SCF calculations at large distance. For  $R=5.85$  Å, the  $R$  distance in the true bridged configuration, this scheme was shown to lead a low-lying ZnBC  $\rightarrow$  BC CT excitation energies of 3.75 eV. This is  $\sim 0.6$  eV larger than our GW-BSE 3.16 eV value found for the model dimer at the same distance.

As analyzed in Ref. 9, the assumption of a distance independent correlation correction to CIS leads to somehow too large excitation energies. This problem was addressed in a recent study<sup>9</sup> where scaled (parametrized) perturbative CIS(D) double excitation corrections to CIS were introduced to account for correlations,<sup>49</sup> reducing the discrepancy with our BSE calculations to about 0.25 eV.<sup>50</sup> While differences in basis size may possibly explain part of the small residual discrepancy,<sup>50</sup> it remains that the comparison of quantum chemistry post-Hartree-Fock correlated techniques, such as second-order Møller-Plesset (MP2) methods (see Note 49), with the present GW-BSE approach, is a current challenge, with MP2 techniques facing scaling and divergency problems for extended systems with large polarizability,<sup>51</sup> while the GW-BSE approach on the contrary still needs further validation for finite size molecules. The present study clearly aims at contributing to that important goal.

In conclusion, we have performed an *ab initio* many-body GW-BSE perturbation theory analysis of the optical transition energies for the ZnBC-BC complex. For the isolated monomers, the calculated GW-BSE Q-bands transition energies are found to be in remarkable agreement with experiment, in particular if one goes beyond the Tamm-Dancoff approximation. In the case of the ZnBC-BC complex, the GW-BSE calculations correctly locate the charge-transfer excitations above the monomer Q-bands transitions. Our CT excitation energies are found to be within less than 0.1 eV from parametrized TDDFT-CAM-B3LYP values for the short range charge transfer in the bridged configuration, but only the GW-BSE formalism can reproduce the correct long distance asymptotic limit. The possibility to study on the same footing, namely without any system-dependent parameter, charge transfer excitation energies at various ranges, both in the vacuum or in a screening environment (solid, solvent, etc.), opens the way to important developments in the study of charge-transfer excitations and energy transfer processes at stake in photosynthetic processes or in organic photovoltaic cells.

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  - <sup>44</sup> M. Grüning, A. Marini, X. Gonze, Nano Lett. **9**, 2820 (2009).
  - <sup>45</sup> E. Livshits, R. Baer, Phys. Chem. Chem. Phys. **9**, 2932 (2007).
  - <sup>46</sup> Takeshi Yanai, David P. Tew, Nicholas C. Handy, Chem. Phys. Lett. **393**, 51 (2004).
  - <sup>47</sup> The BSE approach with static screening is formally equivalent to time-dependent Hartree plus screened exchange. As such, the screening automatically sets the range and strength of the effective Coulomb interaction. In particular, the correct  $1/(\epsilon_M D)$  long-range limit would be correctly described within *GW*-BSE in a medium with macroscopic dielectric constant  $\epsilon_M$  (e.g. in solvent conditions).
  - <sup>48</sup> The *GW*-BSE approach was originally designed for extended semiconductors. See Ref. 23.
  - <sup>49</sup> This approach is described in Ref. 9 as an “excited state analogues of ground state scaled second-order Møller-Plesset (MP2) methods”. The word “scaled” indicates that the implementation relies on scaling parameters educated on various molecules, excluding the ZnBC-BC complex.
  - <sup>50</sup> Value estimated from Fig. 9 of Ref. 9. Calculations in Ref. 9 were performed with a 6-31G\* basis, namely a DZP basis smaller than the TZDP basis used here.
  - <sup>51</sup> For a recent analysis, see: A. Grüneis, M. Marsman, G. Kresse, J. Chem. Phys. **133**, 074107 (2010); and references therein.